

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

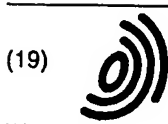
Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 245 700 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
02.10.2002 Bulletin 2002/40

(51) Int Cl.⁷: **C23C 30/00**, C23C 16/40,
C23C 16/36

(21) Application number: **02445036.3**

(22) Date of filing: **15.03.2002**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(72) Inventor: **Ruppi, Sakari**
S-737 44 Fagersta (SE)

(74) Representative: **Taquist, Lennart**
Sandvik AB
Patent Department
811 81 SANDVIKEN (SE)

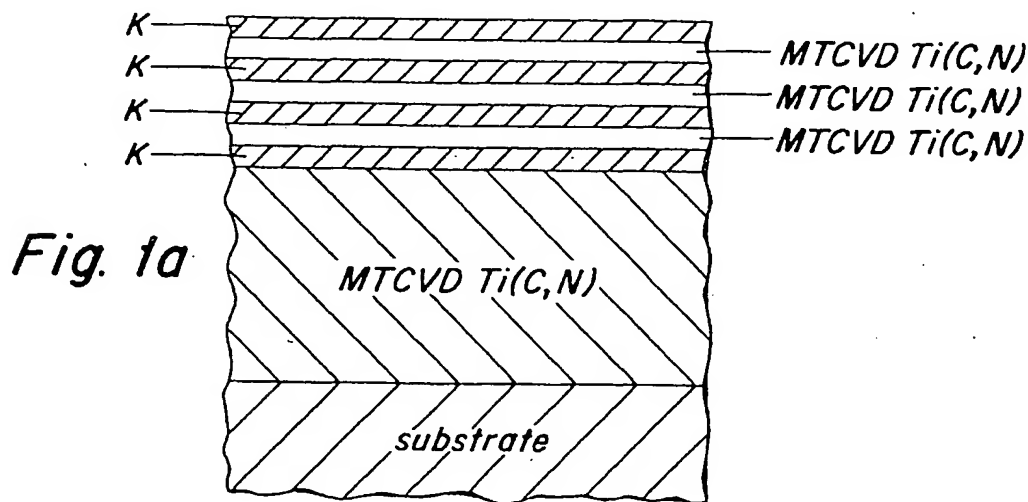
(30) Priority: **27.03.2001 US 817025**

(71) Applicant: **SECO TOOLS AB**
S-773 01 Fagersta (SE)

(54) **Kappa and/or gamma A1203 multi-coating deposited by low temperature CVD**

(57) A coated body having a multi-layer of κ - Al_2O_3 and or γ - Al_2O_3 or TiN applied by MTCVD (Medium Temperature Chemical Vapor Deposition) is disclosed. The multi-layers can be interspersed with layers of Ti(C,N)

which can also be applied by MTCVD. The body which is coated is preferably a cemented carbide, cermet, ceramic and/or high speed steel and may be used as a metal cutting insert.



EP 1 245 700 A1

Description

BACKGROUND OF THE INVENTION

- 5 [0001] Multi-layers of κ - Al_2O_3 and $\text{Ti}(\text{C},\text{O})$ or κ - Al_2O_3 and TiN have proved to exhibit better wear properties than single oxide layers, see U.S. Patent 5,700,569 and U.S. Serial No. 09/717,006.
- [0002] The deposition process of these prior art multi-layers is, however, relatively long and deposition is usually carried out at relatively high temperatures (usually at about 1000°C), resulting in the transformation of kappa-alumina to alpha-alumina. The volume shrinkage encountered in the phase transformation will reduce adhesion of the alumina layers. As a result, adhesion problems in production will occur.
- 10 [0003] It has usually been thought that deposition temperatures of about 1000°C or higher are needed to deposit Al_2O_3 coatings. As shown in the recent U.S. Application Serial No. 09/498,344, Al_2O_3 can be deposited at the deposition temperatures about or exceeding 800°C , but less than 1000°C . Further, it was shown that the two Al_2O_3 phases, κ and γ , could be deposited in a controlled way.
- 15 [0004] It has recently been confirmed that $\text{Ti}(\text{C},\text{N})$ exhibits better wear resistance against crater wear and flank wear in hypoeutectoid steels than TiN (U.S. Serial No. 09/207,687). In recent in-house cutting tests, it has also been found that in hypereutectoid steel, $\text{Ti}(\text{C},\text{N})$ is better than TiN , especially with respect to flank wear. In hyper-eutectic steel, Al_2O_3 is a superior coating material against crater wear. In recent cutting tests in-house, it has also been found that the adhesion of both κ and γ phases to the MTCVD $\text{Ti}(\text{C},\text{N})$ deposited at 800°C is surprisingly good. By depositing κ or γ with MTCVD $\text{Ti}(\text{C},\text{N})$ as a multi-layer, the wear properties of the prior art $\text{TiN}/\text{Ti}(\text{C},\text{O})$ - κ multi-layers could thus be enhanced.
- 20

OBJECTS AND SUMMARY OF THE INVENTION

- 25 [0005] It is an object of this invention to avoid or alleviate the problems of the prior art.
- [0006] It is further an object of this invention to provide enhanced wear properties of $\text{TiN}/\text{Ti}(\text{C},\text{O})$ - κ multi-layers by depositing κ or γ with MTCVD $\text{Ti}(\text{C},\text{N})$ as a multi-layer.
- [0007] In one aspect of the invention there is provided a coated body wherein the coating comprises a multi-layer of γ - Al_2O_3 .
- 30 [0008] In another aspect of the invention there is provided a coated body wherein the coating comprises a multi-layer of κ - Al_2O_3 and/or γ - Al_2O_3 layers interspersed with layers of $\text{Ti}(\text{C},\text{N})$ on a layer of $\text{Ti}(\text{C},\text{N})$.
- [0009] In another aspect of the invention there is provided a coated body wherein the coating comprises a multi-layer of κ - Al_2O_3 and γ - Al_2O_3 , each applied by a chemical vapor deposition at a temperature of from 700 to 900°C .
- [0010] In another aspect of the invention there is provided a coated body wherein the coating comprises a multi-layer of κ - Al_2O_3 and/or γ - Al_2O_3 layers interspersed with layers of $\text{Ti}(\text{C},\text{N})$ on a layer of $\text{Ti}(\text{C},\text{N})$.
- 35 [0011] In yet another aspect of the invention there is provided a coated body wherein the coating comprises a multi-layer of κ - Al_2O_3 and/or γ - Al_2O_3 layers interspersed with layers of $\text{Ti}(\text{C},\text{N})$ on a layer of $\text{Ti}(\text{C},\text{N})$ and with a layer of $\text{Ti}(\text{C},\text{N})$ atop of the said multi-layer.

40 BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Fig. 1 is a representation of a coated body of the present invention including κ - Al_2O_3 multi-layers (Fig. 1a), γ - Al_2O_3 with multi-layers (Fig. 1b) and a mixed γ - and κ - Al_2O_3 multi-layer (Fig. 1c).

45 [0013] Fig. 2 is a representation of a coated body of the present invention useful in cutting of SS1672 (Fig. 2a) and SS2258 (Fig. 2b).

[0014] Fig. 3 shows Scanning Electron Microscope (SEM) images of the cutting edges of single and multi-layer κ - Al_2O_3 coated inserts after turning of 2, 5 and 8 minutes (9 minutes for the multi-layer κ - Al_2O_3 coated insert) of SS2258.

[0015] Fig. 4 shows Scanning Electron Microscope (SEM) images of the cutting edges of single and multi-layer κ - Al_2O_3 coated inserts after turning of 2, 9 and 15 minutes of SS1678.

50

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

[0016] Fig. 1 shows a schematic of the coating layer according to this invention. The coating is composed of the following layers:

55 [0017] 1. MTCVD $\text{Ti}(\text{C},\text{N})$ base layer, deposition temperature 800 - 900°C

[0018] 2. Multi-layer structure consisting of κ - Al_2O_3 (Fig. 1a), γ - Al_2O_3 (Fig. 1b) or both (Fig. 1c), together with MTCVD $\text{Ti}(\text{C},\text{N})$ interlayers, all deposited at a temperature of 800 - 900°C . The wear properties of γ are not yet fully elucidated. However, γ is a less stable phase than κ and can be used only in the uppermost layers of the multi-coating structure

which will be subjected to the shortest annealing during deposition.

[0019] The Al_2O_3 layers in the multi-layer (whether γ or κ) have an individual thickness of from about 0.1 to 3.2 microns, preferably about 0.3 to 1.2 microns. The Ti(C,N) layers in the multi-layer have an individual thickness of from about 0.1 to about 3.2 microns, preferably from about 0.3 to about 1.2 microns. The total thickness of the multi-layer is from about 3 to about 30 microns, preferably from about 5 to 15 microns. The multi-layer may also be deposited onto a Ti(C,N) layer of from about 2 to about 15 microns, preferably from about 3 to 10 microns, which in this instance is the first layer applied onto the body. In addition, a Ti(C,N) layer of the same thickness can be deposited atop the outermost layer of the alumina.

[0020] The body is preferably formed of a cemented carbide, a cermet, a ceramic, or a high speed steel and the coated body is preferably used as a cutting tool in metal cutting operations.

[0021] The γ - and κ - Al_2O_3 layers as well as the Ti(C,N) layers are applied by MTCVD (Medium Temperature Chemical Vapor Deposition). The deposition of the γ - and κ - Al_2O_3 layers utilize the technique described in my copending U.S. Patent Application Serial No. 09/498,334, herein incorporated by reference. In that process, H_2S is added to the otherwise conventional MTCVD techniques and apparatus in amounts greater than 0.7 vol %, generally 0.75 to 1.7 vol %, preferably greater than 1 up to about 1.5 vol %, of the total gaseous mixture.

[0022] The coating process is performed at temperatures of from about 700 to 900°C, preferably 750 to 850°C, at a pressure of from about 50 to 600 mbar, preferably from about 100 to 300 mbar, for a time sufficient to form the coating, generally from about 2 to 10 hours, preferably from about 4 to 8 hours.

[0023] It should be noted that the deposition of Al_2O_3 can be carried out at the same temperature as the MTCVD (Ti(C,N)) layers, resulting in considerably shorter processes (the heating up/cooling down steps are eliminated) and the deposition of the multi-layer is carried out at relatively low temperature, resulting in no phase transformations. As a result, enhanced adhesion will be obtained and production yield will be enhanced. The multi-layer coating can be composed of both κ and γ which can simply be controlled by H_2S . The γ phase which is less stable than κ should be situated in the uppermost part (i.e., top half) of the multi-coating layer, if used; and as shown earlier, MTCVD Ti(C,N) exhibits better wear resistance than TiN . By using Ti(C,N) instead of TiN , crater wear resistance in hypo-eutectic steels and flank wear resistance in hyper-eutectic steels will be enhanced.

[0024] The invention is additionally illustrated in connection with the following Examples which are to be considered as illustrative of the present invention. It should be understood, however, that the invention is not limited to the specific details of the Examples.

EXAMPLE 1

[0025] Tables 1 and 2 show a summary of the wear properties of different coating in SS1672 and SS2258 (hypo- and hyper-eutectic steels, respectively)

Table 1 -

SS1672				
	Crater Wear	Flank Wear	Notch Wear	Deformation
α - Al_2O_3	---	---	++	++
κ - Al_2O_3	---	---	++	+++
TiCN(MTCVD)	++	+++	-	-
TiCN (CVD)	+++	+++	-	-
TiN (CVD)	+	++	++	--
TiC (CVD)	+	+++	-	-

Table 2 -

SS2258				
	Crater Wear	Flank Wear	Notch Wear	Deformation
α - Al_2O_3	+++	--	++	++
κ - Al_2O_3	+++	-	++	+++
TiCN(MTCVD)	--	+++	-	-

Table 2 - (continued)

SS2258				
	Crater Wear	Flank Wear	Notch Wear	Deformation
TiCN (CVD)	--	+++	-	-
TiN (CVD)	--	+	-	--
TiC (CVD)	---	+++	-	-

[0026] As can be seen, the coating material may show very different behaviors in these steels. Consequently, different coating structures have to be developed for SS1672 (thin Al_2O_3 layers + thick Ti(C,N) layers, Fig. 2a) and for SS2258 (thick Al_2O_3 layers + thin Ti(C,N) layers, Fig. 2b) in accordance with the knowledge of the skilled artisan. Schematics of the optimized coating structures for these steel are shown in Figs. 2a and 2b.

EXAMPLE 2

[0027] Cutting tests were performed in SS1672 and SS2258. The coating, according to Fig. 2a, being composed of 6 $\kappa\text{-Al}_2\text{O}_3$ layers interspersed by layers of Ti(C,N), (total multi-layer thickness 7 μm) was tested on SS1672 and a coating deposited according to Fig. 2b, being composed of 5 $\kappa\text{-Al}_2\text{O}_3$ layers interspersed by layers of Ti(C,N) (total multi-layer thickness 7 μm) was tested on SS2258. Cutting tests were also conducted using inserts having single layers of Al_2O_3 , TiN and Ti(C, N) as well as a multi-layer of κ -alumina and TiN were compared. The results are given in Tables 3 and 4.

Table 3 -

SS1672, Cutting Speed 250 m/min		
Coating	Life time/min	Failure Mode
Al_2O_3	11	crater wear
TiN	15	crater wear + notch
TiCN	19	crater wear + notch
Multi κ + TiN	25	crater wear
Multi κ + TiCN	39	crater wear

Table 4 -

SS2258, Cutting Speed 200 m/min		
Coating	Life time/min	Failure Mode
Al_2O_3	15	flank wear
TiN	8	crater wear
TiCN	8	crater wear
Multi κ + TiN	25	flank wear
Multi κ + TiCN	32	flank wear

EXAMPLE 3

[0028] A detailed comparison of the behaviors of a single layer and a multi-layer coating (Fig. 2b) in turning SS2258, is presented in Fig. 3. The multi-layer coating is superior to the single layer SS2258. In this steel, the flank wear is clearly reduced by the Ti(C,N) coatings. It is clear from the SEM micrograph that both crater wear and flank wear resistance of the multi-layer $\kappa\text{-Al}_2\text{O}_3$ coated inserts were superior to those of the single $\kappa\text{-Al}_2\text{O}_3$ coated inserts. In this kind of steel where alumina-coated inserts in general perform well, the effects of the multi-layering is very clear. The lifetime of the insert is drastically increased, in particular at 200 m/min more than about 100%. In ball-bearing steel, SS2258 (hypereutectoid steel), a multi layering results in much more drastically reduced wear than observed earlier

in hypoeutectoid steels (U.S. Patent 5,700,569).

EXAMPLE 4

[0029] A detailed comparison of the behaviors of a single layer and a multi-layer coating (Fig. 2b) in turning of SS1672, is presented in Fig. 4. The multi-layer coating is superior to the single layer also in SS1672. Compared with multilayer κ - Al_2O_3 coatings according to U.S. Patent 5,700,569, multilayers of κ - Al_2O_3 with Ti(C,N) together with reduced thickness of the alumina layers enhanced the performance of the inserts over the prior art. It appears clear from the SEM micrograph that both crater wear and flank wear resistances were superior to those exhibited by the single layer. In this steel, the flank wear is clearly reduced more than earlier observed when multi-layer coatings of κ - Al_2O_3 and Ti(C, O) were investigated (U.S. Patent 5,700,569).

[0030] The principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

Claims

1. A coated body wherein the coating comprises a multi-layer of γ - Al_2O_3 .
2. A coated body wherein the coating comprises a multi-layer of κ - Al_2O_3 applied by a chemical vapor deposition at a temperature of from 700 to 900°C.
3. A coated body wherein the coating comprises a multi-layer of κ - Al_2O_3 and γ - Al_2O_3 , each applied by a chemical vapor deposition at a temperature of from 700 to 900°C.
4. The coated body of any of claims 1, 2 and 3 wherein the said multi-layers of γ - and/or κ - Al_2O_3 are interspersed with layers of Ti(C,N).
5. The coated body of claim 4 wherein the multi-layers of γ and/or κ - Al_2O_3 comprise layers having a thickness of from about 0.1 to about 3.2 microns.
6. The coated body of claim 4 wherein the multi-layers of γ and/or κ - Al_2O_3 comprise layers having a thickness of from about 0.3 to about 1.2 microns.
7. The coated body of claim 4 wherein the layers of Ti(C,N) comprise layers having a thickness of from about 0.1 to about 3.2 microns.
8. The coated body of claim 4 wherein the layers of Ti(C,N) comprise layers having a thickness of from about 0.3 to about 1.2 microns.
9. The coated body of any of claims 1, 2 and 3 wherein a layer of Ti(C,N) is atop the said multi-layers of γ and/or κ - Al_2O_3 .
10. The coated body of claim 3 wherein the γ - Al_2O_3 layers comprise the uppermost alumina layers and the κ - Al_2O_3 layers comprise the innermost alumina layers.
11. The coated body of any of claims 1, 2, and 3 wherein the said multi-layers have a total thickness of from about 3 to about 30 microns.
12. The coated body of claim 11 wherein the said multi-layers have a total thickness of from about 5 to about 15 microns.
13. The coated body of any of claims 1, 2, and 3 wherein the said body is selected from the group consisting of a cemented carbide, cermet, ceramic, high speed steel and mixtures thereof.
14. A metal cutting tool made from the coated body of claim 13.

EP 1 245 700 A1

15. A coated body wherein the coating comprises a multi-layer of $\kappa\text{-Al}_2\text{O}_3$ and/or $\gamma\text{-Al}_2\text{O}_3$ layers interspersed with layers of Ti(C,N) on a layer of Ti(C,N).
- 5 16. A coated body wherein the coated comprises a multi-layer of $\kappa\text{-Al}_2\text{O}_3$ and/or $\gamma\text{-Al}_2\text{O}_3$ layers interspersed with layers of Ti(C,N) on a layer of Ti(C,N) and with a layer of Ti(C,N) atop of the said multi-layer.

10

15

20

25

30

35

40

45

50

55

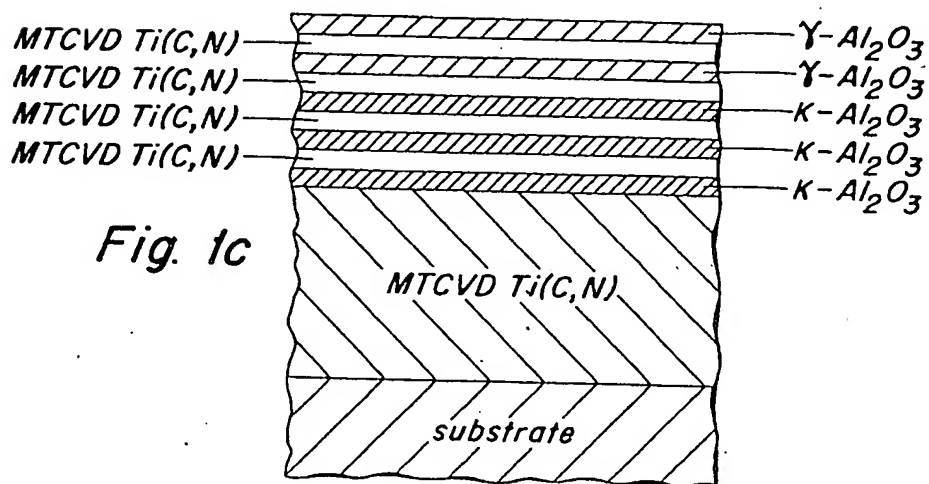
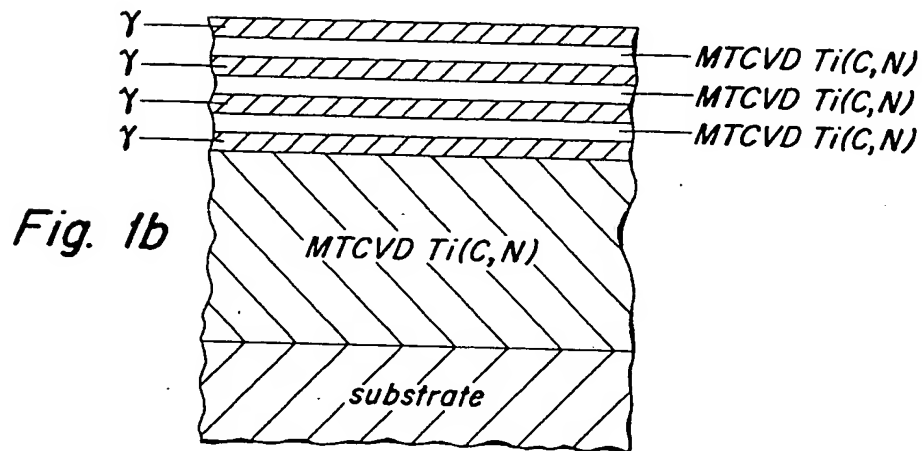
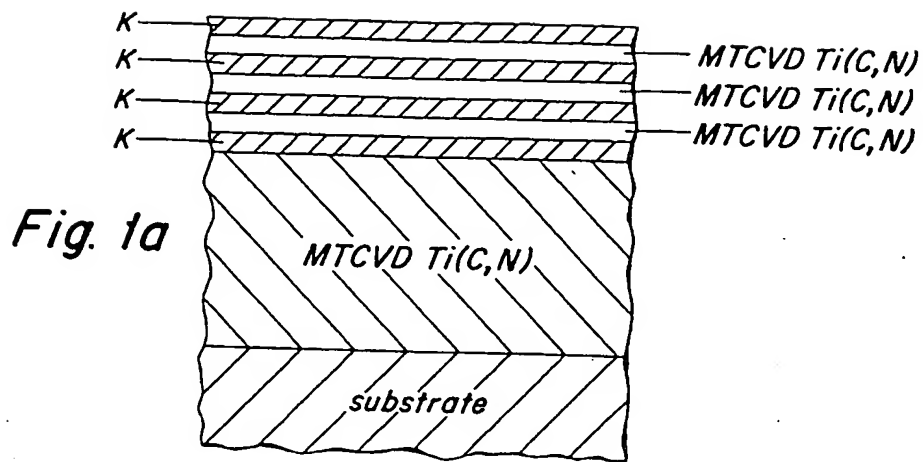


Fig. 2a

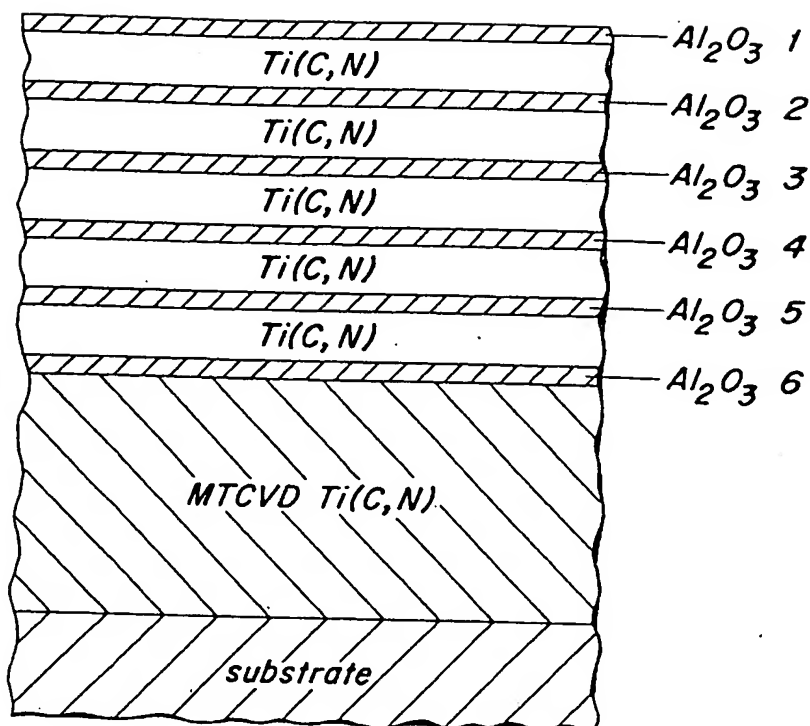
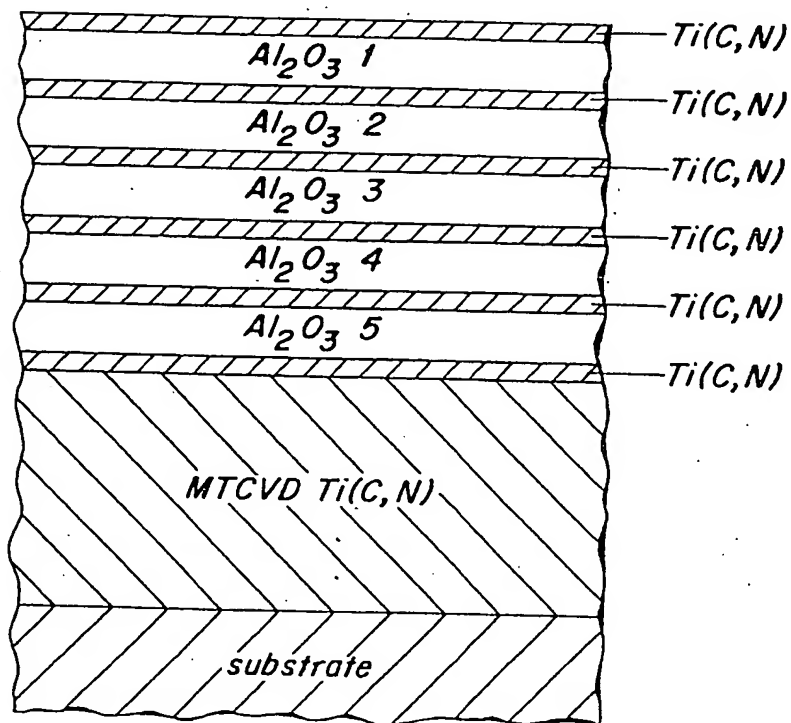
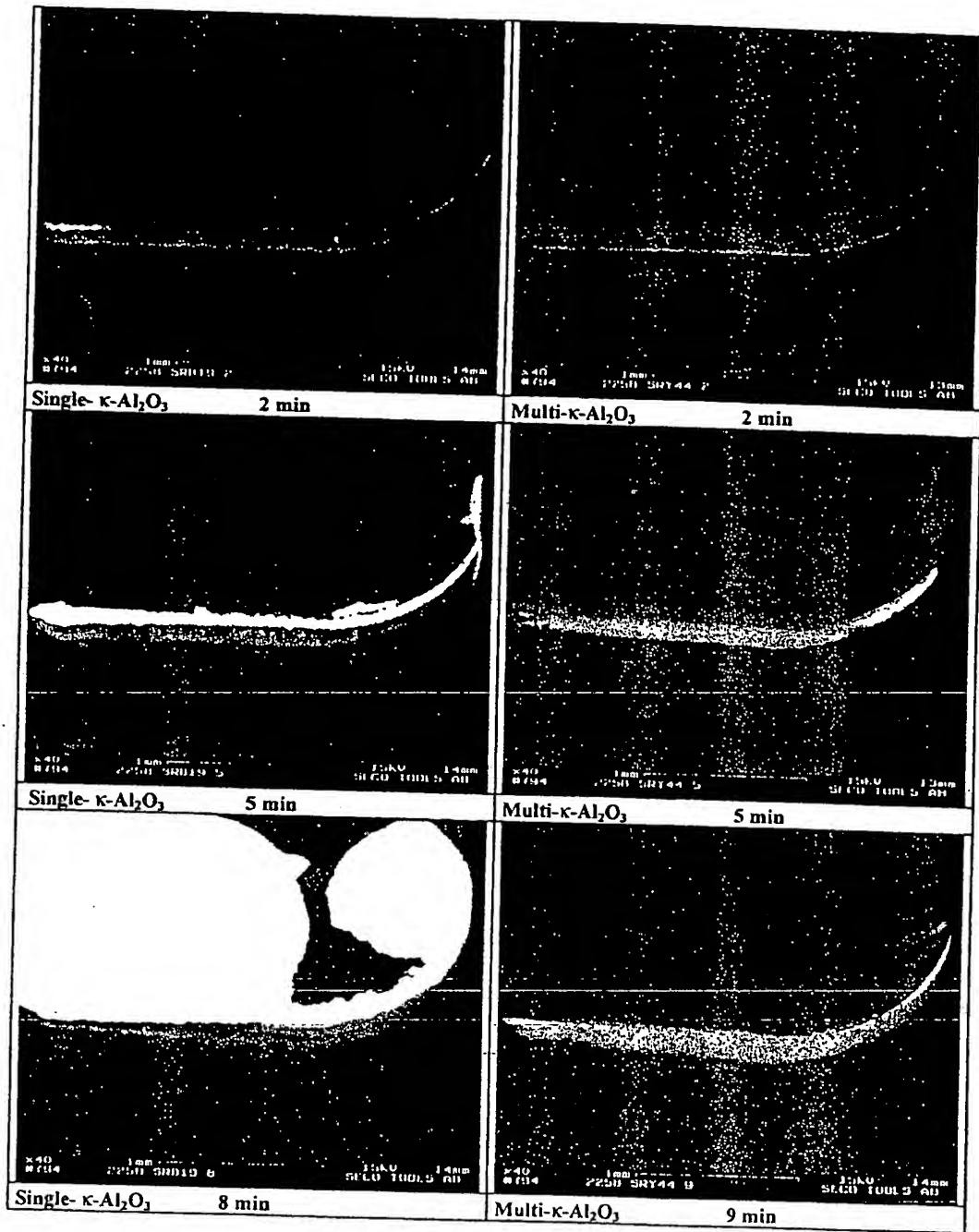


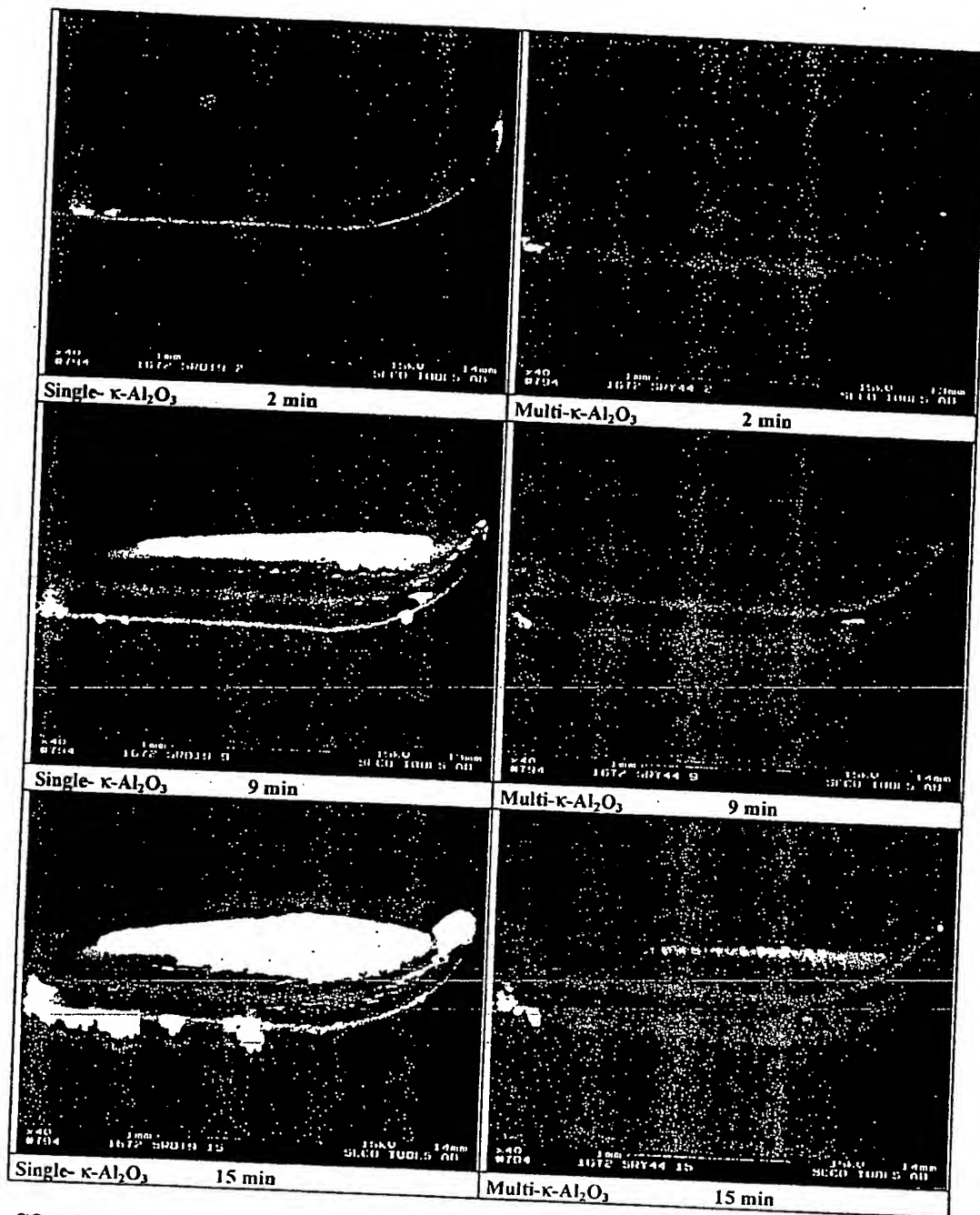
Fig. 2b





SS 2258
 $v_c = 275\text{m/min}$
 $f = 0.4\text{ mm/r}$
 $a_p = 2.5\text{ mm}$

Fig. 3



SS 1672

 $v_c = 250\text{m/min}$, cutting time 2, 9 and 15 min $f = 0.4\text{ mm/r}$ $a_p = 2.5\text{ mm}$

Fig. 4

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 44 5036

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
P,X	EP 1 122 334 A (SECO TOOLS AB) 8 August 2001 (2001-08-08) * claims 2,4; examples *	3,5,7, 10-15	C23C30/00 C23C16/40 C23C16/36
P,X	EP 1 118 688 A (SECO TOOLS AB) 25 July 2001 (2001-07-25) * claims 1,14-19 *	2,4,9, 13-16	
P,X	EP 1 103 635 A (SANDVIK AB) 30 May 2001 (2001-05-30) * paragraph '0025! - paragraph '0033! *	2,4-9, 11-16	
X	WO 99 29921 A (SANDVIK AB) 17 June 1999 (1999-06-17) * claims 1,2,6,7 *	1,4, 11-15	
X	US 5 587 233 A (TABERSKY RALF ET AL) 24 December 1996 (1996-12-24) * column 2-4; claim 7 *	1,4-6, 13,14	
X	EP 0 686 707 A (MITSUBISHI MATERIALS CORP) 13 December 1995 (1995-12-13) * tables 5-8 *	2,5,6,9, 11-14	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C23C
Y	US 4 984 940 A (GRAB GEORGE P ET AL) 15 January 1991 (1991-01-15) * claims; table 1 *	1-16	
Y	US 4 746 563 A (NAKANO MINORU ET AL) 24 May 1988 (1988-05-24) * column 1-5 *	1-16	
Y	US 5 968 595 A (KUTSCHER AASA) 19 October 1999 (1999-10-19) * the whole document *	2,4-16	
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 18 June 2002	Examiner Brisson, O
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

CPO FORM 1503 03.02 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 02 44 5036

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

18-06-2002

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1122334	A	08-08-2001	CN 1316545 A	10-10-2001
			EP 1122334 A1	08-08-2001
			JP 2001254177 A	18-09-2001
EP 1118688	A	25-07-2001	CN 1305880 A	01-08-2001
			EP 1118688 A1	25-07-2001
			JP 2001234344 A	31-08-2001
			US 2002012818 A1	31-01-2002
EP 1103635	A	30-05-2001	EP 1103635 A2	30-05-2001
			JP 2001205505 A	31-07-2001
			SE 9904274 A	26-05-2001
			SE 0000667 A	30-08-2001
WO 9929921	A	17-06-1999	EP 0966551 A1	29-12-1999
			JP 2001513709 T	04-09-2001
			SE 9704631 A	11-06-1999
			WO 9929921 A1	17-06-1999
			US 6333099 B1	25-12-2001
US 5587233	A	24-12-1996	DE 4209975 A1	30-09-1993
			AT 155176 T	15-07-1997
			WO 9320257 A1	14-10-1993
			DE 59306887 D1	14-08-1997
			EP 0632850 A1	11-01-1995
			JP 7505442 T	15-06-1995
EP 0686707	A	13-12-1995	JP 2746036 B2	28-04-1998
			JP 6190605 A	12-07-1994
			EP 0686707 A1	13-12-1995
US 4984940	A	15-01-1991	AU 631199 B2	19-11-1992
			AU 5194590 A	22-10-1990
			BR 9001433 A	09-04-1991
			CA 1327277 A1	01-03-1994
			DE 69013678 D1	01-12-1994
			DE 69013678 T2	24-05-1995
			DE 463000 T1	09-04-1992
			EP 0463000 A1	02-01-1992
			ES 2029983 T1	16-10-1992
			JP 6061646 B	17-08-1994
			JP 4504085 T	23-07-1992
			KR 121790 B1	12-11-1997
			MX 172507 B	17-12-1993
			WO 9011156 A1	04-10-1990

EPO FORM P/049

For more details about this annex see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 02 44 5036

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

18-06-2002

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4746563 A	24-05-1988	JP 1462114 C	14-10-1988
		JP 60238481 A	27-11-1985
		JP 62006748 B	13-02-1987
		AU 578950 B2	10-11-1988
		AU 4208585 A	21-11-1985
		DE 3580121 D1	22-11-1990
		EP 0162656 A2	27-11-1985
		KR 8904787 B1	27-11-1989
US 5968595 A	19-10-1999	SE 514695 C2	02-04-2001
		AT 208439 T	15-11-2001
		BR 9603082 A	05-05-1998
		CN 1148100 A	23-04-1997
		DE 69616669 D1	13-12-2001
		DE 69616669 T2	02-05-2002
		EP 0753602 A1	15-01-1997
		IL 118792 A	17-02-2000
		JP 9136202 A	27-05-1997
		SE 9502638 A	15-01-1997
		US 5902671 A	11-05-1999

EPO FORM P0436

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82